

Fragile-to-Strong Crossover in Supercooled Liquids Remains Elusive

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Transport properties of glass forming liquids change markedly around an onset temperature T_o . For temperatures T above T_o , these properties depend little with T , while for $T < T_o$ these properties are *super-Arrhenius* – varying *faster* than exponentially in $1/T$. Upon lowering temperature significantly further, theory [1] predicts that reversible transport in a supercooled liquid, if it can be observed, will ultimately cross over from super-Arrhenius to Arrhenius temperature variation. But this so-called “fragile-to-strong” (FS) crossover at a temperature $T_x < T_o$ has proved difficult to observe because most bulk fluids fall out of equilibrium at a glass transition temperature T_g that is higher than T_x . Yet Mallamace et al [2] report the observation of T_x for a large number of supercooled liquids. In truth, they observe the onset to supercooled behavior, and the reported values of T_x are poor lower-bound estimates to onset temperatures T_o . This fact is consistent with transport decoupling appearing only below temperatures identified with the crossover in Ref. [2].

To illustrate this understanding about Ref. [2], I graph data in Fig. 1 for two typical supercooled liquids. The data is compared with the parabolic form for transport property τ (denoting either relaxation time or viscosity),

$$\log_{10} \tau = \log_{10} \tau_o + J^2 \left(\frac{1}{T} - \frac{1}{T_o} \right)^2, \quad T < T_o, \quad (1)$$

and with the straight-line fit that would be associated with the Arrhenius temperature dependence. I consider data for liquid salol in my Fig. 1A. This is the same liquid and the same temperature range considered in Fig. 1A of Ref. [2]. The two figures are strikingly different, due in part to Ref. [2] showing an outlying data set [3] that is discredited by subsequent studies on the same liquid [4]. Unlike Fig. 1A of Ref. [2], my graph shows excellent agreement between reproducible experimental data and the parabolic form.

My Fig. 1B considers a second liquid to illustrate that the behavior for salol is consistent with that of other systems. Indeed, the parabolic form, with its three material properties τ_o , J and T_o , has been used to collapse data for more than 50 supercooled liquids [4] over the entire supercooled temperature range, $T_o > T > T_g$, and this form appears to be universal for all fragile glass formers [5]. I have chosen to show two specific examples in this Letter to contrast with the obscuring clutter of data analyzed with six-parameter fits in Figs. 1C and 2 of Ref. [2].

The two graphs presented here and those presented

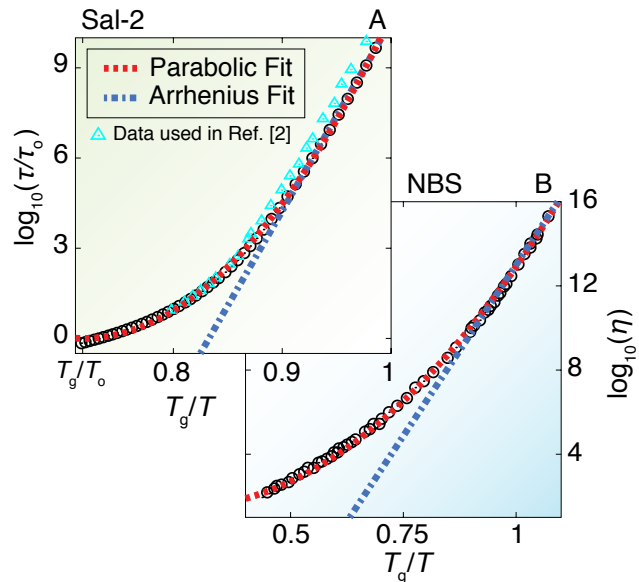


FIG. 1: Transport properties as a function of T_g/T for two typical supercooled liquids. Black circles in Panels A and B represent experimental data considered in [4]. Labeling here is consistent with [4] – that is to say that Sal-2 and NBS refer to the same experimental measurements and fit parameters as in Table 1 of [4]. Red dashed line is the fit parabolic form for $T < T_o$, as in [4]. Blue dashed line represents Arrhenius fit for lowest T points [2]. In Panel A, relaxation time, τ , of Salol where $T_g = 221$ K is the glass transition temperature where $\log(\tau/s) = 2$. In Panel B, viscosity, η , of NBS where $T_g = 708$ K is the glass transition temperature where $\log(\eta/\text{Poise}) = 13$. It is generally assumed that $\tau \propto \eta$, and, with this assumption, Panel A includes data used in Ref. [2] (triangles).

in Refs. [4] and [5] indicate that all reliable reversible transport data for bulk supercooled liquids appear to be smooth, with no compelling feature suggesting a change from parabolic to linear behavior. Rather, it seems that the FS crossover reported in [2] results from confusing T_o with T_x , and how, over a limited range, a parabola looks like a straight line. The search for the FS crossover in bulk materials therefore remains elusive.

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